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JPAB,EPAB,DWPI	persulfate same ((ammnium or sodium or potassium) adj phosphate) same (sulfuric or phosphoric)	1	L13
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L6: Entry 10 of 13 File: USPT Mar 13, 1979

DOCUMENT-IDENTIFIER: US 4144119 A
TITLE: Etchant and process

ABPL:
This invention is directed to an etchant and to a process for its use. The etchant comprises sulfuric acid activated with hydrogen peroxide or the synergistic combination of hydrogen peroxide and molybdenum. The etchant is characterized by a source of phosphate ions as an inhibitor against attack on tin, especially immersion tin, as well as several other metals such as nickel and alloys of nickel such as gold alloys. The etchant is especially useful for etching copper and its alloys in the presence of a tin etch resist, and therefore, provides a new procedure for the fabrication of printed circuit boards using immersion tin as an etch resist.

BSPR:
This invention relates to an etchant comprising sulfuric acid activated with hydrogen peroxide or a synergistic combination of hydrogen peroxide and hexavalent molybdenum, a process for using the same, especially in the manufacture of printed circuit boards and novel articles made therewith.

BSPR:
The activation of relatively dilute mineral acids with an oxygen release compound is known in the art and described, for example, in Plating, "Surface Treatment of Metals with Peroxygen Compounds", Vol. 42, pg 561 (1955). In the Plating publication, it is taught that mineral acids such as sulfuric acid, nitric acid, acetic acid and phosphoric acid may be activated with oxygen release compounds such as hydrogen peroxide or other peroxy, persulfate or perborate compounds. The oxygen release compound enhances the etch rate thereby permitting a decrease in the concentration of acid.

BSPR:
Activation of dilute sulfuric acid with hydrogen peroxide is most attractive due to low cost and ease of electrolytic copper recovery from the spent etchant prior to disposal. However, the utility of such hydrogen peroxide etching solutions is reduced somewhat due to catalyzed decomposition of hydrogen peroxide caused by etched metal ions or other transition metal ions in solution and a slow etch rate, typically 1.4 mils of copper from 1 ounce copper clad laminate in 10-25 minutes at 120.degree. F. To enhance etch rate, more concentrated solutions of hydrogen peroxide have been used, but concentrated peroxide solutions are hazardous to health and safety. In addition, such etchants have not been successfully used with tin dissimilar metal etch resists because they attack tin, especially immersion tin.

BSPR:
The etchant of the above-noted copending application Ser. No. 822,002 is an improvement over the acid etchants activated with peroxide as disclosed in the prior art. However, the etchants of said application are not desirably used in certain specific processes for etching copper, including its alloys, where the copper is etched in the presence of tin as a metal etch resist such as in chemical milling of copper and in the manufacture of printed circuit boards. The limitation in the use of the etchant is a consequence of attack by the etchant on immersion tin and certain electroplated tins resulting in either the complete dissolution of the tin or partial removal of some of the tin and discoloration of the remaining tin.

BSPR:

In accordance with the subject invention, it has been found that the addition of phosphate ions to sulfuric acid etchants activated with hydrogen peroxide or a combination of hydrogen peroxide and molybdenum inhibits the attack of the etchant on the tin etch resists. Hence, the etchant of the invention may be used for etching copper in contact with a tin etch resist. Accordingly, processes for use of the etchant, in accordance with the invention, comprise providing a tin etch resist in a desired configuration over copper and contacting the same with the etchant of the invention for a period of time sufficient to remove unwanted copper. The tin etch resist can be either immersion tin or electroplated tin. The process is especially useful for the manufacture of printed circuit boards and in the chemical milling of copper.

BSPR:
a new etchant for etching copper in the presence of a tin etch resist;

BSPR:
new processes for chemical milling and for the manufacture of printed circuit boards characterized by etching copper in a desired configuration utilyzing tin as a metal etch resist; and

BSPR:
new articles of manufacture comprising a copper substrate which has portions removed by etching and other portions not removed protected by a coating of a tin etch resist.

DEPR:
Sulfuric acid is used for purposes herein because it is the most economical, provides best results and yields copper sulfate upon saturation which is readily recovered by lowering the temperature of the etchant,. However, other acids may be used in admixture with the sulfuric acid for specific desired results. Therefore, the term sulfuric acid as used herein means sulfuric acid alone or in mixture with other acids in lesser amounts where desired.

DEPR:
A molybdenum compound is preferably added to the etchant as a synergistic co-oxidant with the hydrogen peroxide to exalt the etch rate. The particular molybdenum compound used does not appear to be critical provided it is sufficiently soluble in solution and is oxidized to a form that etches copper in the etchant environment. Preferably, the molybdenum is added as hexavalent molybdenum but may be added in a lower valence form as the peroxide will oxidize it to its higher valence forms. believed to be hexavalent molybdenum and/or permolybdate. The preferred molybdenum compound is sodium molybdate. Other useful molybdenum compounds include ammonium molybdate and molybdic acid.

DEPR:
The concentration of the molybdenum compound is not critical, it having been found that for immersion etching, the etch rate increases with small additions of molybdenum and levels off as concentration increases. For etching copper, some exaltation of the etch occurs when the molybdenum concentration is as low as 0.01 moles per liter (as molybdenum metal) and rapidly increases as the concentration increases to about 0.1 to 0.15 moles per liter. Thereafter, the etch rate continues to increase, but at a less rapid rate to a maximum rate obtained at between about 0.4 to 1.0 moles per liter dependent upon numerous variables such as temperature, peroxide content, dissolved metal content and the like. for spray etching an exalted rate occurs at higher concentrations of molybdenum than for immersion etching.

DEPR:
It is of interest to note that in an etchant stabilized with an arylsulfonic acid, as the concentration of molybdenum increases up to about 0.75 moles per liter, the normal peroxide consumption is reduced. This is suggestive that the molybdenum is the primary etchant and the peroxide consumption is not due to etching, but rather to oxidation of the reduced form of molybdenum. In accordance with this invention, a compound that yields phosphate ions is added to the etchant to inhibit attack on tin etch resists. The preferred compound is phosphoric acid or an alkali phosphate. Typical examples of phosphate in addition to phosphoric acid include sodium phosphates and potassium phosphates. The concentration of the phosphate in the etchant is not cirtical, minor amounts inhibiting attack on tin to some degree and larger amounts providing greater

protection up to a maximum where attack again appears. In general, the amount used is that amount that substantially eliminates the attack and this is dependent upon the composition of the etchant and the conditions under which it is used. Preferably, the concentration of the phosphate varies between 0.1 and 2.5 moles per liter (as phosphate) and more preferably, between 0.25 and 1.5 moles per liter.

DEPR:
Using the etchant of this invention to etch copper, at 120.degree. F., the bath will dissolve about 70 to 80 grams of copper per liter. Maintaining the hydrogen peroxide concentration within 50-100% of its initial bath makeup and at all times in an amount sufficient to maintain a ratio of the peroxide to molybdenum of at least 1:1 when molybdenum is used permits continued operation until saturation with dissolved copper. Allowing the bath to cool to room temperature induces crystallization of copper compounds which may be recovered by filtration dependent upon the acid used. Readjustment in the concentration of the components of the etch solution makes the same suitable for reuse.

DEPR:
It is of interest to note that as etching proceeds, where molybdenum is present in the etchant, at the interface of the etchant and copper, a deep blue layer forms which is the color of molybdenum in a lower valence form. This is suggestive that molybdenum has been reduced by oxidation of the copper layer and dissolution of the same. This deep blue color will persist at the interface unless the etchant is stirred. If stirred, the color is lost which is further suggestive that the reduced molybdenum has been reoxidized to hexavalent form by the peroxide. Moreover, if the peroxide is not present in solution, etching will proceed but only for a short period of time and thereafter, etching stops. While etching is taking place, the entire solution becomes deep blue establishing that molybdenum does etch copper but is not reoxidized in the absence of the peroxide.

DEPR:
In a typical process for the manufacture of printed circuit boards, a suitable base material is selected such as copper clad epoxy. Holes are drilled at appropriate locations on the board and the walls of the holes are metallized such as with copper to provide electrical contact between the two surfaces of the base material. Methods for metallization are known and include the steps of cleaning, catalyzing and electroless copper deposition.

DEPR:
Following metallization of the holes, utilizing a process known as pattern plating, a conductor pattern is formed on the copper by application of an organic resist material which may be either a photoresist or a screen resist dependent upon design and definition. The resist coats the copper that is not part of the conductor pattern and leaves the copper bare in a conductor pattern. The thickness of the conductor pattern is then increased using electroless and/or electrolytic copper plating procedures. Following the steps of copper plating, a dissimilar metal etch resist such as solder is applied over the copper in the conductor pattern to protect the same from subsequently applied etchants, the organic resist is removed exposing the unwanted copper (not part of the conductor pattern), and the unwanted copper is dissolved with a suitable etchant for the copper such as that disclosed herein while the conductor pattern is protected from the etchant by the dissimilar metal etch resist. Typically, the dissimilar metal etch resist is selected not only for its ability to withstand the etchant, but also for its solderability so the electrical connections can be soldered directly to the etch resist.

DEPR:
A novel process using the etchants of this invention comprises plating tin over copper as a metal etch resist rather than another metal etch resist heretofore used in the art such as solder. The tin is plated over those portions of the copper to be protected from the etchant and not over those portions to be removed. For example, in a process for the fabrication of a printed circuit board such as described above, an organic resist would be coated over the copper to define a copper conductor pattern in a manner known to the art. The copper in the conductor pattern would be plated with tin, the organic resist removed and the unwanted copper not protected by the tin etched with the etchant of this invention. Thereafter, the tin could, if desired, be reflowed by heating to a

temperature above its melting point. Other components of an electrical assembly may then be joined directly to the tin in a manner similar to soldering.

DEPR:
An article manufactured by a process using tin such as described above is novel because it is believed that tin has not earlier been successfully used as an etch resist. Therefore, copper in a defined pattern, such as an image pattern, coated with tin is believed to comprise a new article of manufacture. Also considered to be a new article of manufacture is copper coated with tin in a defined pattern, as described above, having electrical or other connections directly to the tin.

DEPR:
A preferred tin for a process as described above is immersion tin where tin is deposited by displacement of copper of the copper substrate without the use of an external source of electricity. Immersion tin compositions are disclosed, for example, in U.S. Pat. No. 3,303,029 incorporated herein by reference. A preferred immersion tin composition comprises Example 1 of said patent.

DEPR:
The above illustrates that the concentration of the phosphoric acid has little effect on etch rate.

DEPR:
Using the formulations of Examples 1 through 6, copper panels measuring 3 inches by 3 inches and having a copper thickness of 1.4 mils had one-half of their surface coated with an immersion tin deposit. The immersion tin used was a formulation identified as LT-27 of Shipley Company Inc. The immersion tin was coated onto the copper by immersing the cleaned surface in the LT-27 formulation for 5 minutes at 170.degree. F. The results obtained are as set forth in the following table:

DEPR:
Other sources of phosphate were substituted for phosphoric acid in Example 1 with the resulting formulations used to etch a 3".times.3" copper clad epoxy panel having 1/2 of its surface area coated with LT-27 tin. The phosphates used, the amounts and the results are set forth below:

DEPR:
A printed circuit board is prepared from a copper clad G-10 substrate using the following sequence of steps:

DEPR:
(b) Metallize the walls of the holes by electroless plating including the steps of catalysis with a catalyst such as Catalyst 6F of Shipley Company Inc., accelerate with a mild acid solution and electrolessly plate copper such as with copper mix CP-74 of Shipley Company Inc.

DEPR:
(d) Electroplate copper to full desired thickness,

DEPR:
(e) Apply immersion tin over the exposed copper.

DEPR:
(g) Remove exposed copper by immersion of the epoxy coated board in the etchant of Example 4 until all unwanted copper is dissolved.

DETL:
______________________________________ Constituent 1 2 3 4 5 6
______________________________________ Sulfuric acid (50%) 200 200 200 200 200 200 ml.sup.(1) Hydrogen Peroxide 100 100 100 100 100 100 (35%) ml Sodium Molybdate gm 10 10 10 10 10 10 Phenolsulfonic acid gm 16 16 16 16 16 16 Phosphoric acid (85%) ml 0 10 10 50 100 250 Water to 1 liter Time.sup.(2) to etch 1 gm copper at 120.degree. F (min) 6 6 6 6 6 6
______________________________________ .sup.(1) Battery grade or better. .sup.(2) By immersion of substrate in etchant.

DETL:
______________________________________ Phosphoric acid Example No. Content in

Etch (ml) Attack on Tin ______ 7 0 Tin fully dissolved 8 10 Tin fully dissolved 9 25 Tin fully dissolved 10 50 No attack 11 100 No attack 12 250 Some attack on edges ______

DETL:

______ Amount Constituent 13 14 ______ Sulfuric Acid (50%) ml.sup.(1) 200 200 Hydrogen Peroxide (35%) ml 100 100 Phenolsulfuric acid gm 16 16 Phosphoric acid (85%) ml 50 250 Water to 1 liter Time.sup.(2) to etch copper at 120.degree. F (min) 18 19 Attack on immersion tin LT-27 none Partial on edges ______ .sup.(1) Battery grade or better. .sup.(2) By immersion in etchant of 1.4 mil copper clad epoxy substrate measuring 3".times.3" having 1/2 its surface coated with LT-27 tin.

DETL:

______ Example No. Phosphate Amount Attack on Tin ______ 15 Ammonium phosphate 25 Partial 16 Ammonium phosphate 50 None 17 Ammonium phosphate 10 None 18 Sodium phosphate 30 Partial 19 Sodium phosphate 60 None 20 Sodium phosphate 120 None

______

CLPR:

1. A sulfuric acid etchant activated with an oxidant combination of hydrogen peroxide and molybdenum, the hydrogen peroxide being present in an amount sufficient to oxidize the molybdenum and provide sustained etching and the molybdenum being present in an amount sufficient to exalt the etch rate to a rate in excess of that achievable by the peroxide alone, said etchant being characterized by the inclusion of phosphate ions in an amount sufficient to inhibit the attack of the etchant on tin.

CLPR:

4. The etchant of claim 1 where the source of phosphate is phosphoric acid.

CLPR:

5. A process for etching copper metals coated in part with tin comprising the step of contact of said copper with the etchant of claim 1.

CLPR:

6. The process of claim 5 wherein the tin defines a pattern on the surface of said copper.

CLPR:

9. A process for making a printed circuit board by etching a conductor pattern on a copper surface comprising defining a conductor pattern by coating said copper with tin in said conductor pattern and etching copper not coated with tin with the etchant of claim 1.

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L8: Entry 17 of 34 File: USPT Aug 18, 1992

DOCUMENT-IDENTIFIER: US 5139923 A
TITLE: Method for improving adhesion of a resist layer to a metallic layer and electrolessly plating a wiring pattern thereon

BSPR:
This invention relates to a method of wiring a printed circuit board and particularly to a method of wiring a printed circuit board suitable for high-density and fine wiring.

BSPR:
In accordance with a recent trend toward an increase in the density and fineness of a printed circuit board, various proposals have been made in order to attain this purpose. One of the proposals is a method which comprises masking a copper clad laminate as a starting material at the portion other than the portion to be wired with a photoresist for plating and subjecting only the portion to be wire to plating, e.g., electroless copper plating for wiring. In this method, the resist for plating and metallic layer portion unnecessary for wiring (i.e., the metallic layer portion below the resist for plating) is removed after the completion of copper plating of the portion to be wired

BSPR:
However, the adhesion between the copper clad laminate and the photoresist for plating is generally poor, which raises a problem that it is impossible to conduct satisfactory wiring because the resist for plating is peeled off during plating. In particular, when fine wiring is intended, the occurrence of the peeling is a serious problem. In order to solve this problem, for example, Japanese Patent Laid-Open No. 48831/1986 has proposed a method which comprises mechanically rubbing the surface of a copper clad laminate etc. with pumice, applying an adhesion promoting agent, such as benzotriazole, to the rubbed surface, and masking the desired portion with a photoresist for plating. This method is one which has given a solution to the problem that the resist for plating is peeled from the surface of the undercoat copper layer during plating. Further, a method in which the same effect can be attained by adding an adhesion promoting agent such as benzotriazole to a photoresist for plating, has been proposed and has made it possible to solve the problem of the above-described peeling.

BSPR:
Although copper having high conductivity is generally used for pattern plating, the metal for pattern plating is not limited to this alone. A suitable metal used as the second metallic layer and having a larger ionization tendency than the metal for the above-described pattern plating when copper is used for pattern plating is at least one element selected from among aluminum, zinc, tin, chromium, iron, nickel, and cobalt or an alloy containing at least one of these elements in an amount of at least 5% by weight. Further, as described above, at least one element selected from among noble metals, such as gold and platinum, (i.e., gold, silver, and platinum group elements) is suitable as a metal for use in the second metallic layer which hardly forms an oxide.

BSPR:
When the first metallic layer is made of copper and the second metallic layer is made of the above-described element or alloy, the thickness of the second metallic layer is usually preferably 0.01 to 1 .mu.m. However, even when the thickness is below than the above-described range, an effect is attained to some extent as far as a major portion of the first metallic layer is covered with the second metallic layer. In general, when about 10% or more of the surface of the

undercoat layer of the second metallic layer is exposed and is not covered with the second metallic layer, the adhesion of the resist for plating unfavorably becomes poor. On the other hand, when the second metallic layer is excessively thick, the roughness of the surface is decreased, which brings about a lowering in the adhesion of the resist for plating. The upper limit of the thickness of the second metallic layer in the case of the above-described combination is about 1 .mu.m. Further, in general, no problem is caused when the thickness of the second metallic layer is 1 .mu.m or less not only in the case of the above-described combination of the metallic layer but also in the case of other combinations. As described above, in the above-described combination of the metallic layer, the thickness of the second metallic layer is preferably 0.01 to 1 .mu.m. However, in the case of other combinations of the metallic layer, it is preferred to find an optimum condition of the thickness of the second metallic layer by forming the second metallic layer plating and the resist for plating on the first metallic layer and then actually determining the blistering and peeling of the resist.

BSPR:
The present invention causes neither peeling of the resist for plating during pattern plating nor influence on the plating film. This enables desired wiring in accordance with the circuit pattern and the circuit drawn by the resist for plating, thus making it possible to form fine wiring.

DEPR:
FIG. 1A shows the state of an insulating board 1 provided with a metallic layer 2 and having a hole 3 bored in a desired portion. The first metallic layer 2 is generally made of copper and may be one commercially available in the form of a copper clad laminate. The insulating board 1 may also be made of a wide variety of materials such as commercially available glass epoxy laminate, glass polyimide laminate, and paper phenolic laminate. In the step shown in FIG. 1A, if necessary, it is also possible to previously form a circuit through etching of the metallic layer 2.

DEPR:
However, the formation of the thin metallic layer 4 ensures more reliable wiring although the number of steps is disadvantageously increased. The thin metallic layer 4 can be formed by any of dry processes, such as vapor deposition, and wet processes, such as plating. However, the wet process is thought to be advantageous from the standpoint of mass productivity. Examples of the wet process include a method in which the thin metallic layer is formed only by electroless copper plating, a method in which electroplating is conducted after electroless plating, or a method in which in general, a catalyst for electroless copper plating is placed in the hole 3 for activation and direct electroplating is conducted. There is no particular limitation with respect to the thickness of the thin metallic layer 4. However, as described above, a thickness of 2 .mu.m to 10 .mu.m generally suffices for the thin metallic layer 4.

DEPR:
Then, a second metallic layer 5 is formed on the thin metallic layer 4 or the metallic layer 2. FIG. 1C shows a state in which the second metallic layer 5 has been formed on the thin metallic layer 4. A thickness of 1 .mu.m or less suffices for the second metallic layer. An effect can be attained even when the thickness is such that the color o the metal constituting the second metallic layer is slightly observed, for example, when the thickness is about 0.01 .mu.m. However, no satisfactory effect can be attained when the thin metallic layer 4 constituting the undercoat of the second metallic layer 5 or the surface of the metallic layer 2 is exposed over a wide area (about 10% or more). In the combination other than that of the above-described materials when the first metallic layer is made of copper, the thickness varies depending upon the roughness of the surface and the kind of the metal, which makes it necessary to find out an optimum condition for practical use. Examples of the method of forming the second metallic layer include dry processes, such as vapor deposition, sputtering, and ion plating and wet processes, such as electroless plating, electroplating, and substitution plating. The second metallic layer can be formed by any of the above-described methods.

DEPR:
When the thin metallic layer 4 or metallic layer 2 is made of copper, the following coarsening method is effective in improving the evenness of the

coarsening and the bonding strength. One of the coarsening methods comprises coarsening the surface of the copper with a treating solution containing an etching agent, e.g., a persulfate such as ammonium persulfate or sodium persulfate, or cupric chloride. When the surface of the copper is to be further coarsened, the coarsening with the treating solution containing the above-described etching agent is followed by the oxidation of the coarsened surface with a chlorite, such as sodium chlorite or potassium chlorite, and then a treatment with a reducing treatment solution to reconvert the resulting copper oxide into the metallic copper. This treatment enables further coarsening of the surface of the copper. A treating solution containing an amineborane compound, such as dimethylamineborane, is particularly useful as the reducing treatment solution. Further, the surface which has been oxidized with the above-described chlorite or the like may be electrically subjected to cathodic reduction. Either of the above-described methods may be used in the present invention

DEPR:
Then, wiring is conducted by providing a pattern plating layer 7 as shown in FIG. 1E. Copper plating is best suited as the pattern plating for wiring from the viewpoint of conductivity. Examples of the copper plating include electroless copper plating, electro-copper plating, and a combination of them. When the hole 3 is small, the electroless copper plating is advantageous from the viewpoint of the throwing power ratio of the through hole plating. When the pattern plating layer 7 is to be formed, the second metallic layer 5 in an exposed state may be left as it is. However, when zinc or the like is used for the second metallic layer, it is preferred from the viewpoint of corrosion resistance to remove the second metallic layer In this case, the second metallic layer can be removed with an inorganic acid or the like.

DEPR:
After the completion of the step shown in FIG. 1E, the resist for plating and the unnecessary metallic layer are removed by an ordinary method, thereby forming final wiring In one example of the well known method, soldering plating is further conducted on the pattern plating layer to form a resist for etching. Subsequently, the above-described resist for plating 6 is removed. The above-described second metallic layer 5, the thin metallic layer 4, and the metallic layer 2 other than the etching resist formed on the circuit are etched away with the etching resist. When the metallic layer 2, the thin metallic layer 4 and the second metallic layer 5 are thin, differential etching may directly be conducted to form wiring without conducting the soldering plating. When the soldering plating is conducted, if necessary, it may be removed in the final step FIG. 1F is a cross-sectional view of a state of a structure in which all of the above-described steps have been completed, i.e., a final structure.

DEPR:
Although the above description has been made mainly by referring to the pattern plating in the case where the metallic layer is present on the whole underlying surface, the present invention can also quite equally be applied to the method which comprises previously forming a wiring pattern as a first metallic layer on the surface of an insulating board and conducting electroless plating only on the hole and necessary wiring portion, such as a pad for a through hole, to form a printed circuit board.

DEPR:
Further, the present invention can also be applied to the case where the above-described double-side printed circuit board is multilayered to prepare a multilayered printed circuit board

DEPR:
A double-side copper clad laminate having a board thickness of 0.1 mm and a copper thickness of 9 .mu.m was degreased with an alkali, washed with water, and then treated for 1 min with a soft etching solution (30.degree. C.) prepared by dissolving 200 g of ammonium persulfate and 5 ml of 98% sulfuric acid in water so as to have a final volume of 1 l. The treated laminate was washed with water and then plated with zinc in an electro-zinc plating bath (Zincalux; a product of Schering Corp.) for 1 min at an apparent current density of 1 A/dm.sup.2, thereby forming a second metallic layer having a thickness of 0.2 .mu.m. The plated laminate was washed with water and dried, and a 50 .mu.m-thick photosensitive dry film SR-3200 (trademark of a product of Hitachi Chemical Co., Ltd.) was laminated thereon, followed by exposure and development to prepare a desired negative

wiring pattern for use as a resist for plating. The thus-treated laminate was further treated with 3% sulfuric acid for 2 min, washed with water and then plated with copper in an electroless copper plating solution (71.degree. C.) having the following composition to form 30 .mu.m-thick copper plating as pattern plating, thereby conducting wiring:

DEPR:
Holes were bored in the necessary portion of a double-side copper clad laminate having a substrate thickness of 1 mm and a copper thickness of 18 .mu.m. Then, the laminate was degreased with an alkali, washed with water, and treated for 1 min with a soft etching solution (30.degree. C.) prepared by dissolving 200 g of ammonium persulfate and 5 ml of 98% sulfuric acid in water so as to have a final volume of 1 l. The treated laminate was washed with water, treated with 15% hydrochloric acid for 1 min and then with a catalyst solution (HS101B; a product of Hitachi Chemical Co., Ltd.) at 20.degree. C. for 5 min, washed with water, treated with 3% hydrochloric acid at 20.degree. C. for 5 min, and then washed with water, thereby conducting activation. The activated laminate was plated in an electroless copper plating solution (70.degree. C.) having the following composition to form a 5 .mu.m-thick copper plating layer:

DEPR:
The plated laminate was washed with water and then plated with zinc in an electro-zinc plating bath (Zincalux; a product of Schering Corp.) for 1 min at an apparent current density of 1 A/dm.sup.2, thereby forming a second metallic layer having a thickness of 0.2 .mu.m. Then, the plated laminate was washed with water and dried, and a 50 .mu.m-thick photosensitive dry film SR-3200 was laminated thereon, followed by exposure and development to prepare a desired negative wiring pattern for use as a resist for plating. The laminate having the resist for plating was treated with 3% sulfuric acid for 2 min, washed with water and then plated with copper in an electro-copper plating solution comprising 60 g/l of copper sulfate and 200 g/l of sulfuric acid at 30.degree. C. and 3 A/dm.sup.2 for 50 min to form a copper pattern plating layer having an average thickness 33 .mu.m, thereby forming a circuit. Thereafter, the resist for plating and the unnecessary metallic layer were removed in the same manner as that of Example 1.

DEPR:
Holes were bored in the necessary portion of a double-side copper clad laminate having a board thickness of 1 mm and a copper thickness of 18 .mu.m. Then, the laminate was degreased with an alkali, washed with water, and treated for 1 min with a soft etching solution (30.degree. C.) prepared by dissolving 200 g of ammonium persulfate and 5 ml of 98% sulfuric acid in water so as to have a final volume of 1 l. The treated laminate was washed with water, treated with 15% hydrochloric acid for 1 min, immersed in a catalyst solution HS101B (trademark of a product of Hitachi Chemical Co., Ltd.) at 20.degree. C. for 5 min, washed with water, treated with 3% hydrochloric acid at 20.degree. C. for 5 min, and then washed with water, thereby conducting activation. The surface of the copper was coarsened by buff brushing and pumice brushing t have a satin finish, washed with water, and subjected to electro-zinc plating in the same manner as that of Example 1 to form a second metallic layer having a thickness of 0.2 .mu.m, followed by laminating with a photosensitive dry film, exposure, development, and electroless copper plating, thereby forming a circuit. Thereafter, the resist for plating and the unnecessary metallic layer were removed in the same manner as that of Example 1.

DEPR:
Holes were bored in the necessary portion of a double-side copper clad laminate having a board thickness of 1 mm and a copper thickness of 18 .mu.m. Then, the laminate was degreased with an alkali, washed with water, and treated for 1 min with a soft etching solution (30.degree. C.) prepared by dissolving 200 g of ammonium persulfate and 5 ml of 98% sulfuric acid in water so as to have a final volume of 1 l. The treated laminate was washed with water and then plated for 2 min with gold at an apparent current density of 1 A/dm.sup.2 in an electro-gold plating bath prepared by dissolving 7 g of potassium gold syanide and 20 g of potassium cyanide in water so as to have a final volume of 1 l, thereby forming a second metallic layer having a thickness of 0.8 .mu.m. The gold-plated laminate was sufficiently washed with water, immersed in 15% hydrochloric acid for 1 min, immersed in a catalyst solution (HS101B; a product of Hitachi Chemical Co., Ltd.) at 20.degree. C. for 5 min, washed with water, treated with 3% hydrochloric acid at 20.degree. C. for 5 min, and then washed with water, thereby conducting

activation. The activated gold-plated laminate was washed with water and dried, followed by laminating with a photosensitive dry film, exposure, development, and electroless copper plating in the same manner as that of Example 1, thereby forming a circuit. Thereafter, the resist for plating and the unnecessary metallic layer were removed in the same manner as that of Example 1.

DEPR:
Holes were bored in the necessary portion of a double-side copper clad laminate having a board thickness of 1 mm and a copper thickness of 18 .mu.m. Then, the laminate was degreased with an alkali, washed with water, and treated for 1 min with a soft etching solution (30.degree. C.) prepared by dissolving 200 g of ammonium persulfate and 5 ml of 98% sulfuric acid in water so as to have a final volume of 1 l. The treated laminate was washed with water, immersed in 15% hydrochloric acid for 1 min, immersed in a catalyst solution (HS101B; a product of Hitachi Chemical Co., Ltd.) at 20.degree. C. for 5 min and washed with water. The treated laminate was immersed for 2 min in a treating solution (75.degree. C.) comprising 90 g/l of sodium chlorite, 15 g/l of sodium hydroxide and 30 g/l of sodium phosphate and washed with water. The treated laminate was then immersed for 1 min in an aqueous solution containing 6 g/l of dimethylamineborane and 5 g/l of sodium hydroxide (40.degree. C.) to reduce the resulting oxide film and sufficiently washed with water, followed by electro-zinc plating, laminating with a photosensitive dry film, exposure, development, and electroless copper plating, in the same manner as that of Example 1, thereby forming a circuit. The thickness of the second metallic layer comprising zinc was 0.01 .mu.m. The resist for plating and the unnecessary metallic layer were removed in the same manner as that of Example 1.

DEPR:
Holes were bored in the necessary portion of a double-side copper clad laminate having a board thickness of 1 mm and a copper thickness of 18 .mu.m. Then, the laminate was degreased with an alkali, washed with water, and treated for 1 min with a soft etching solution (30.degree. C.) prepared by dissolving 200 g of ammonium persulfate and 5 ml of 98% sulfuric acid in water so as to have a final volume of 1 l. The treated laminate was washed with water, immersed in 15% hydrochloric acid for 1 min, immersed in a catalyst solution HS101B at 20.degree. C. for 5 min, washed with water, treated with 3% hydrochloric acid at 20.degree. C. for 5 min, and then washed with water, thereby conducting activation. The activated laminate was plated in an electroless copper plating solution (70.degree. C.) having the following composition to form a 5 .mu.m-thick copper plating layer:

DEPR:
The plated laminate was washed with water and then treated for 20 sec with an etching solution (45.degree. C.) containing 500 ml/l of hydrochloric acid and 40 g/l of cupric chloride (dihydrate), immediately washed with water, and further immersed in an oxidizing solution (70.degree. C.) comprising 90 g/l of sodium chlorite, 15 g/l of sodium hydroxide, and 30 g/l of sodium phosphate. The treated copper-plated laminate was immersed for 1 min in a reducing solution (30.degree. C.) comprising 6 g/l of dimethylamineborane and 5 g/l of sodium hydroxide to reduce the resulting oxide film, followed by washing sufficiently with water and plating with zinc in an electro-zinc plating bath (Zincalux; a product of Schering Corp.) at room temperature for 5 min at an apparent current density of 0.5 A/dm.sup.2, thereby forming a second metallic layer having a thickness of 0.02 .mu.m. Then, the zinc-plated laminate was washed with water and dried, and a 50 .mu.m-thick photosensitive dry film SK-3200 (trademark of a product of Hitachi Chemical Co., Ltd.) was laminated thereon, followed by exposure and development to prepare a desired negative wiring pattern. The laminate having the negative pattern was treated with 3 % sulfuric acid for 5 min, washed with water and then subjected to pattern plating of about 30 .mu.m in a electroless copper plating solution (72.degree. C.) having the following composition to conduct wiring:

DEPR:
A circuit was formed in the same manner as that of Example 6, except that a second metallic layer having a thickness of 0.03 .mu.m was formed by conducting tin plating in an electro-tin plating bath (20.degree. C.) having the following composition at an apparent current density of 0.5 A/dm.sup.2 for 5 min instead of the electro-zinc plating conducted in Example 6:

DEPR:

Wiring was conducted in the same manner as that of Example 6, except that a second metallic layer was formed by vapor deposition of aluminum on the surface of the board to form a layer having a thickness of about 0.1 .mu.m instead of the electro-zinc plating conducted in Example 6 and the removal of aluminum on the plating surface was conducted with a treating solution having the following composition instead of the treatment with sulfuric acid after formation of the resist for plating:

DEPR:
Wiring was conducted in the same manner as that of Example 6, except that a second metallic layer was formed by vapor deposition of chromium on the surface of the board to form a layer having a thickness of about 0.1 .mu.m instead of the electro-zinc plating conducted in Example 6 and the complete removal of chromium on the plating surface was conducted with a hydroxy alkaline aqueous potassium ferricyanide solution instead of the treatment with sulfuric acid after the formation of the resist for plating.

DEPR:
Holes were bored in the necessary portion of a double-side copper clad laminate having a board thickness of 1 mm and a copper thickness of 35 .mu.m. Then, the laminate was subjected to buff brushing and pumice brushing to coarsen the surface thereof. The coarsened laminate was washed with water and dried, and a photosensitive dry film having a thickness of 35 .mu.m (Laminar GSI; a product of Dynachem Corp.) was then laminated thereon, followed by exposure and development, thereby forming a circuit pattern. The patterned laminate was subjected to etching with an aqueous cupric chloride solution acidified with hydrochloric acid to form a surface circuit. The laminate having the surface circuit was washed with water, and the remaining dry film in the form of a circuit was then removed with methylene chloride. The surface was coarsened by buff brushing and treated for 1 min with a soft etching solution (30.degree. C.) prepared by dissolving 200 g of ammonium persulfate and 10 ml of sulfuric acid in water to have a final volume of 1 l. The treated laminate was then washed with water, immersed in 15% hydrochloric acid for 1 min, immersed in a catalyst solution (HS101B; a product of Hitachi Chemical Co., Ltd.) at 20.degree. C. for 5 min, washed with water, further immersed in 15% hydrochloric acid, and washed with water, thereby conducting the activation. The activated laminate was then immersed in an electroless tin plating bath LT-26 (trademark of a product of Shipley Co.) at 85.degree. C. for 5 sec to form a second metallic layer having a thickness of 0.08 .mu.m. The laminate having the second metallic layer was washed with water and dried, and a photosensitive dry film SR-3200 having a thickness of 35 .mu.m was laminated thereon, followed by exposure and development to expose only the portion to be wired. The laminate was then treated with 3% sulfuric acid for 5 min, and the exposed portion was subjected to electroless copper plating under the same conditions as those of Example 1, thereby completing intended wiring.

DEPR:
Holes were bored in the necessary portion of a double-side copper clad laminate having a board thickness of 1 mm and a copper thickness of 35 .mu.m. Then, the laminate was subjected to buff brushing and pumice brushing to coarsen the surface thereof. The coarsened laminate was washed with water and dried, and a photosensitive dry film having a thickness of 35 .mu.m (Laminar GSI; a product of Dynachem Corp.) was then laminated thereon, followed by exposure and development, thereby forming a circuit pattern. The patterned laminate was subjected to etching with an aqueous cupric chloride solution acidified with hydrochloric acid to form a surface circuit. The laminate having the surface circuit was washed with water, and the remaining dry film in the form of a circuit was then removed with methylene chloride. The surface was coarsened by buff brushing and treated for 1 min with a soft etching solution (30.degree. C.) prepared by dissolving 200 g of ammonium persulfate and 10 ml of sulfuric acid in water to have a final volume of 1 l. The treated laminate was then washed with water, immersed in 15% hydrochloric acid for 1 min, immersed in a catalyst solution HS101B (a product of Hitachi Chemical Co., Ltd.) at 20.degree. C. for 5 min, washed with water, further immersed in 15% hydrochloric acid, and washed with water, thereby conducting the activation. The activated laminate was immersed for 2 min in an oxide film forming treatment solution (75.degree. C.) comprising 90 g/l of sodium chlorite, 15 g/l of sodium hydroxide, and 30 g/l of sodium phosphate and then washed with water. The treated laminate was immersed for 1 min in a reducing solution (40.degree. C.) comprising 6 g/l of dimethylamineborane and 5 g/l of sodium hydroxide to reduce the resulting oxide film. The laminate was then

sufficiently washed with water, followed by immersion in an electroless nickel plating bath (90.degree. C.) having the following composition for 5 min, thereby forming a second metallic layer comprising a nickel plating layer having a thickness of 0.1 .mu.m:

DEPR:
Holes were bored in the necessary portion of a double-side copper clad laminate having a board thickness of 1 mm and a copper thickness of 35 .mu.m. Then, the laminate was degreased with an alkali, washed with water, and treated for 1 min with a soft etching solution (30.degree. C.) prepared by dissolving 200 g of ammonium persulfate and 10 ml of sulfuric acid in water to have a final volume of 1 l. Thereafter, the treated laminate was immersed for 2 min in an oxide film forming treatment solution (75.degree. C.) comprising 90 g/l of sodium chlorite, 15 g/l of sodium hydroxide, and 30 g/l of sodium phosphate and further washed with water. The treated laminate was then subjected to electrolytic reduction in an electrolytic solution comprising 100 g/l of Na.sub.2 SO.sub.4 and 10 g/l of NaOH. The laminate was washed with water and then plated with nickel in an electroplating bath (30.degree. C.) having the following composition at an apparent current density of 0.5 A/dm.sup.2 for 1 min to form a second metallic layer having a thickness of 0.003 .mu.m:

DEPR:
As described above, in Examples 1 to 12, intended excellent printed circuit boards were prepared by removing the second metallic layer and the copper foil layer other than those of the wired portion according to an ordinary method described in Example 1.

DEPL:
Subsequently laminating with a photosensitive dry film, exposure, development, and electroless copper plating were conducted under the same conditions as those of Example 1, thereby completing intended wiring.

DEPL:
The laminate having the second metallic layer was washed with water, and a photosensitive dry film having a thickness of 35 .mu.m (Laminar GSI; a product of Dynachem Corp.) was then laminated thereon, followed by exposure and development, thereby forming a resist for a circuit pattern. The metal of the portion other than the portion of the circuit pattern was removed by etching to conduct intended wiring. The remaining photosensitive dry film in the form of a circuit was then removed with methylene chloride. The resulting laminate was washed with water, immersed in 15% hydrochloric acid for 1 min, immersed in a catalyst solution (HS101B; a product of Hitachi Chemical Co., Ltd.) at 20.degree. C. for 5 min, and washed with water. The washed laminate was then dried, and a photosensitive dry film SR-3200 having a thickness of 35 .mu.m was laminated thereon, followed by exposure and development to expose only the portion to be wired. Then, the laminate was treated with 3% sulfuric acid for 5 min, followed by electroless copper plating of the exposed portion under the same conditions as those of Example 1, thereby completing intended wiring.

DETL:
tin sulfate 30 g/l sulfuric acid 100 ml/l additive (Ronastan; a product of 30 ml/l Meltex Corp.)

CLPR:
1. A method for improving the adhesion of a resist material on an insulating board having a first metallic layer on the surface thereof and for providing a wiring pattern by electroless plating with copper, comprising the steps of:

CLPR:
7. A method according to claim 1, wherein said first metallic layer has a circuit pattern prior to the formation of the resist for plating and the circuit portion is further formed by electroless plating.

CLPR:
9. A method according to claim 1, wherein said first metallic layer comprises copper.

CLPR:

10. A method according to claim 9, wherein the surface of said first metallic layer made of copper is oxidized and then reduced for coarsening.

CLPR:
12. A method according to claim 9, wherein a thin copper layer is formed over said first copper metallic layer which constitutes an undercoat of said second metallic layer.

CLPR:
13. A method according to claim 12, wherein said thin copper layer is formed by electroplating or electroless plating.

CLPV:
a) depositing a second metallic layer of at least one element, or an alloy containing at least 5% by weight of at least one element, selected from the group consisting of aluminum, zinc, tin, chromium, iron, nickel and cobalt, said second metallic layer having a higher ionization tendency than that of copper which is to be electroless plated and that of said first metallic layer, on said first metallic layer, causing said resist material to adhere better thereto than said first metallic layer;

CLPV:
c) electroless plating a wiring pattern with copper on the areas of said second metallic layer not deposited with said resist material.

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L8: Entry 3 of 34 File: USPT Feb 1, 2000

DOCUMENT-IDENTIFIER: US 6020029 A
TITLE: Process for treating metal surfaces

ABPL:
A process for treating metal surfaces that includes first contacting the metal surface with a particular acidic peroxide adhesion promoting composition, followed by contacting that metal surface with an alkaline solution. This treatment is particularly suitable for treating metal surfaces used in printed circuit multilayer construction.

BSPR:
This invention relates to an improvement to the process of providing innerlayer integrity in printed circuit multilayer board construction by the use of an acidic peroxide treatment composition also containing a corrosion inhibitor with the preferable inclusion of a halide ion source and the optional inclusion of water soluble polymers. In particular, the present invention relates to use of an alkaline solution treatment after the acidic peroxide treatment to treat metal surfaces in printed circuit multilayer board construction.

BSPR:
Printed circuits containing one or more circuitry innerlayers are in prominent use today as demand increases for further and further weight and space conservation in electronic devices.

BSPR:
In the typical fabrication of a multilayer printed circuit, patterned circuitry innerlayers are first prepared by a process in which a copper foil-clad dielectric substrate material is patterned with resist in the positive image of the desired circuitry pattern, followed by etching away of the exposed copper. Upon removal of the resist, there remains the desired copper circuitry pattern.

BSPR:
An alternate approach to the formation of a multilayer printed circuit board is through additive or surface laminer circuitry techniques. These techniques begin with a non-conductive substrate, upon which the circuit elements are additively plated. Further layers are achieved by repeatedly applying an imageable coating upon the circuitry and plating further circuit elements upon the imageable coating.

BSPR:
It has long been known that the strength of the adhesive bond formed between the copper metal of the circuitry innerlayers and the cured pre-preg layers, or other non-conductive coatings, in contact therewith leaves something to be desired, with the result that the cured multilayer composite or the coating is susceptible to delamination in subsequent processing and/or use. In response to this problem, the art developed the technique of forming on the copper surfaces of the circuitry innerlayers (before assembling them with pre-preg layers into a multilayer composite) a layer of copper oxide, such as by chemical oxidation of the copper surfaces. The earliest efforts in this regard (so-called "black oxide" adhesion promoters) produced somewhat minimal improvement in the bonding of the circuitry innerlayers to the dielectric substrate layers in the final multilayer circuit, as compared to that obtained without copper oxide provision. Subsequent variations on the black oxide technique included methods wherein there is first produced a black oxide coating on the copper surface, followed by post-treatment of the black oxide deposit with 15% sulfuric acid to produce a "red oxide" to serve as the adhesion promoter, such as disclosed by A. G. Osborne, "An Alternate

Route To Red Oxide For Inner Layers", PC Fab. August, 1984, as well as variations involving direct formation of red oxide adhesion promoter, with varying degrees of success being obtained. The most notable improvement in this art is represented in the U.S. Pat. Nos. 4,409,037 and 4,844,981 to Landau, the teachings both of which are incorporated herein by reference in their entirety, involving oxides formed from relatively high chlorite/relatively low caustic copper oxidizing compositions, and producing substantially improved results in circuitry inner layer adhesion.

BSPR:
As earlier noted, the assembled and cured multilayer circuit composite is provided with through-holes which then require metallization in order to serve as a means for conductive interconnection of the circuitry layers of the circuit. The metallizing of the through-holes involves steps of resin desmearing of the hole surfaces, catalytic activation, electroless copper depositing, electrolytic copper depositing, and the like. Many of these process steps involve the use of media, such as acids, which are capable of dissolving the copper oxide adhesion promoter coating on the circuitry innerlayer portions exposed at or near the through hole. This localized dissolution of the copper oxide, which is evidenced by formation around the through-hole of a pink ring or halo (owing to the pink color of the underlying copper metal thereby exposed), can in turn lead to localized delamination in the multilayer circuit.

BSPR:
The art is well aware of this "pink ring" phenomenon, and has expended extensive effort in seeking to arrive at a multilayer printed circuit fabrication process which is not susceptible to such localized delamination. One suggested approach has been to provide the adhesion promoting copper oxide as a thick coating so as to retard its dissolution in subsequent processing simply by virtue of sheer volume of copper oxide present. This turns out to be essentially counter-productive, however, because the thicker oxide coating is inherently less effective as an adhesion promoter per se. Other suggestions relating to optimization of the pressing/curing conditions for assembling the multilayer composite have met with only limited success.

BSPR:
Other approaches to this problem involve post-treatment of the copper oxide adhesion promoter coating prior to assembly of circuitry innerlayers and pre-preg layers into a multilayer composite. For example, U.S. Pat. No. 4,775,444 to Cordani discloses a process in which the copper surfaces of the circuitry innerlayers are first provided with a copper oxide coating and then contacted with an aqueous chromic acid solution before the circuitry innerlayers are incorporated into the multilayer assembly. The treatment serves to stabilize and/or protect the copper oxide coating from dissolution in the acidic media encountered in subsequent processing steps (e.g., through-hole metallization), thereby minimizing pink ring/delamination possibilities.

BSPR:
U.S. Pat. No. 4,642,161 to Akahoshi et al., U.S. Pat. No. 4,902,551 to Nakaso et al., and U.S Pat. No. 4,981,560 to Kajihara et al., and a number of references cited therein, relate to processes in which the copper surfaces of the circuitry innerlayers, prior to incorporation of the circuitry innerlayers into a multilayer circuit assembly, are first treated to provide a surface coating of adhesion-promoting copper oxide. The copper oxide so formed is then reduced to metallic copper using particular reducing agents and conditions. As a consequence, the multilayer assembly employing such circuitry innerlayers will not evidence pink ring formation since there is no copper oxide present for localized dissolution, and localized exposure of underlying copper, in subsequent through-hole processing. As with other techniques, however, processes of this type are suspect in terms of the adhesion attainable between the dielectric substrate layers and the metallic copper circuitry innerlayers. This is particularly so in these reduction processes since the circuitry bonding surface not only is metallic copper, but also presents the metallic copper in distinct phases (i.e. (1) copper-from-reduction-of-copper oxide over (2) copper of the copper foil) which are prone to separation/delamination along the phase boundary.

BSPR:
U.S. Pat. Nos. 4,997,722 and 4,997,516 to Adler similarly involve formation of a

copper oxide coating on the copper surfaces of circuitry innerlayers, followed by treatment with a specialized reducing solution to reduce the copper oxide to metallic copper. Certain portions of the copper oxide apparently may not be reduced all the way to metallic copper (being reduced instead to hydrous cuprous oxide or cuprous hydroxide), and those species are thereafter dissolved away in a non-oxidizing acid which does not attack or dissolve the portions already reduced to metallic copper. As such, the multilayer assembly employing such circuitry innerlayers will not evidence pink ring formation since there is no copper oxide present for localized dissolution, and localized exposure of underlying copper, in subsequent through-hole processing. Here again, however problems can arise in terms of the adhesion between the dielectric layers and metallic copper circuitry innerlayers, firstly because the bonding surface is metallic copper, and secondly because the metallic copper predominately is present in distinct phases (i.e., (1) copper-from-reduction-of-copper oxide over (2) copper of the copper foil), a situation prone to separation/delamination along the phase boundary.

BSPR:
U.S. Pat. No. 5,289,630 to Ferrier et al., the teachings of which are incorporated herein by reference in their entirety, reveals a process whereby an adhesion promotion layer of copper oxide is formed on the circuit elements followed by a controlled dissolution and removal of a substantial amount of the copper oxide in a manner which does not adversely affect the topography.

BSPR:
U.S. Pat. No. 5,869,130, to Ferrier entitled "Process For Improving Adhesion of Polymeric Materials to Metal Surfaces" describes a process for improving the adhesion of polymeric materials to a metal surface, especially copper or copper alloy surfaces in the production of multilayer printed circuits. The process described in this patent application provides for contacting the metal surface with an adhesion-promoting composition comprising (a) an oxidizer; (b) an acid; (c) a corrosion inhibitor; (d) a source of halide ions; and (e) optionally, a water soluble polymer. That process provided excellent adhesion between the metallic and polymeric surfaces (i.e. the circuitry and the intermediate insulating layer), while eliminating or minimizing pink ring and operating economically, as compared to above noted conventional processes.

BSPR:
However, it has been found that the use of acidic peroxide treatment solutions, while giving good peel strength and stability of copper laminated to fiberglass filled resin, allows the occurrence of some flaws on further processing of the laminated board to create a finished printed circuit board. Thus, with some resin systems, particularly lower T.sub.g materials, drilling removes a small quantity of organic material from the surface of the etch treated copper at the point where the drill intersects with the copper layer; this phenomenon is called "wedge". Further processing the drilled board through the chemical steps of preparing and plating the board creates a small area at the treated copper surface around the drilled hole where the coating is attacked and removed, creating a phenomenon called "pink ring". This area of pink ring is much smaller than the pink ring observed in standard oxide processing to prepare copper surfaces for lamination. Nevertheless, in this area of attack small areas of resin contracting from the copper surface can be observed after floating the board in molten solder. Although these areas of resin contraction (called "resin voids") may not be sufficient cause for rejection of the board they are still a concern.

DEPR:
The present invention is particularly suitable for treating copper surfaces with a combination of an acidic peroxide adhesion-promoting composition followed by an alkaline treatment.

DEPR:
The present process is particularly suited to the manufacture of multilayer printed circuit boards. Thus, in this application, the metal circuitry (usually copper) of the innerlayers is treated with the adhesion-promoting composition proposed herein. After the foregoing treatment followed by, water rinsing, further treatment in the alkaline solution proposed herein, and further water rinsing, the innerlayers are bonded together with polymeric materials such as pre-pregs or imageable dielectrics, resulting in the multilayer printed circuit board.

DEPR:
The metal surface to be treated may comprise a variety of metals such as copper, nickel, iron and alloys of each of the foregoing. However, the process of the invention produces the best results when the metal surfaces comprise copper or copper alloys. The polymeric material may be a variety of polymeric materials including pre-preg materials, imageable dielectrics, photoimageable resins, soldermasks, adhesives or polymeric etch resists.

DEPR:
The oxidizer used in the adhesion-promoting composition may comprise any oxidizer which is capable of oxidizing the metal surface in the matrix of the adhesion-promoting composition. The inventors have found hydrogen peroxide and persulfates to be particularly preferred oxidizers for use in the process of the invention, with hydrogen peroxide being the most preferred oxidizer. The concentration of the oxidizer in the adhesion-promoting composition may range from 6 to 60 grams per liter but is preferably from 12 to 30 grams per liter.

DEPR:
The acid utilized in the adhesion-promoting composition may be any acid which is stable in the matrix, however, the inventors have found mineral acids to be particularly preferred. Sulfuric acid is especially preferred. The concentration of the acid in the adhesion-promoting composition may range from 5 to 360 grams per liter but is preferably from 70 to 110 grams per liter.

DEPR:
After the acidic oxidant treatment, the metal surface is treated with an alkaline solution. The preferred alkaline solution is an aqueous alkaline solution of alkali metal hydroxide (e.g. sodium hydroxide or potassium hydroxide); alkali metal carbonates (e.g. sodium carbonate or potassium carbonate); alkali metal phosphates (e.g. sodium phosphate or potassium phosphates); or amines or mixtures of those chemicals. The preferred amount of such chemicals in the aqueous solution will depend upon the particular chemical employed as well as the exact use involved. Most preferably an aqueous solution of sodium or potassium hydroxide is used as the alkaline treatment, with the concentration of sodium or potassium hydroxide ranging from 2 to 150 grams per liter, most preferably from 25 to 50 grams per liter. Contact may be made by immersion, conveyorized flood or spray, however conveyorized flood is preferred. Contact time may range from 20 seconds to 10 minutes but 1 to 3 minutes is preferred. Contact temperature may range from room temperature to 160.degree. F. but 65 to 100.degree. F. is preferred. This alkaline treatment reduces the number of flaws in the finished laminated product.

DEPR:
After a cleaning step, panels with copper foil completely covering the surface on both sides were treated with an adhesion promoting solution containing:

DEPR:
Samples of copper clad panels and one ounce foil were treated with the adhesion promoting solution as in the Comparative Example; however, the panels were not dried after the final rinse. They were immersed in an aqueous solution of 38 g/L sodium hydroxide at 70.degree. F. for thirty seconds, rinsed thoroughly and dried. The treated panels and foil were then baked, laminated and processed as in the Comparative Example. After cross sectioning and soldering the following results were observed:

DEPL:
Treatment was provided for in a conveyorized flood machine. The parts were rinsed and dried. A one ounce copper foil was also treated to be pressed for measurement of the peel strength of the coating following lamination. After this treatment the panels and foils were covered with a uniform dark, purple/pink coating. The panels were baked thirty minutes in air at 110.degree. C. and laminated with Nelco N4205-2 1080B stage material (T.sub.g approximately 140.degree. C.) and two cap sheets of two ounce zinc treated foil to create a finished panel containing four innerlayers. The treated foil was also laminated in a similar fashion against a treated panel. After lamination, the panels containing innerlayers were drilled and processed for plating through the following standard plated through hole cycle:

DETL:
____________________________________ Sulfuric acid 5% by Volume Hydrogen Peroxide (50%) 5% by Volume Benzotriazole 5 gr/l Carbowax MPEG 2000 3 gr/l Sodium Chloride 40 mg/l Water Balance ____________________________________

DETL:
____________________________________ MacDermid 9204, 110.degree. F.* 5 minutes Cold Water Rinse 2 minutes MacDermid 9275, 165.degree. F.* 15 minutes Cold Water Rinse 1 minute Cold Water Rinse 2 minutes MacDermid 9279, 110.degree. F.* 5 minutes Cold Water Rinse 2 minutes MacDermid Conditioner 90, 120.degree. F.* 5 minutes Cold Water Rinse 5 minutes MacDermid G-4 Microetch, 85.degree. F.* 1 minute Cold Water Rinse 1 minute MacDermid 93 Predip* 1 minute MacDermid 95 Activator* 5 minutes Cold Water Rinse 1 minute Cold Water Rinse 2 minutes MacDermid 97 Accelerator, 110.degree. F.* 2.5 minutes Cold Water Rinse 2 minutes MacDermid M-85 Electroless 30 minutes Copper* Cold Water Rinse 2 minutes MacDermid 9271 Acid Cleaner* 2 minutes Cold Water Rinse 2 minutes MacDermid G-4 Microetch* 15 seconds Cold Water Rinse 2 minutes 10% Sulfuric Acid 1 minutes MacDermid 9241 Acid Copper, 20 40 minutes ASF* Cold Water Rinse 2 minutes ____________________________________ *Note These products are available from MacDermid, Incorporated, 245 Freight Street, Waterbury, CT. 06702. MacDermid is a trademark of MacDermid, Incorporated. These products were prepared and operated according to the manufacturer's published instructions for printed circui plated throughhole operation.

CLPR:
2. The process according to claim 1 wherein the oxidizer is selected from the group consisting of hydrogen peroxide and persulfates.

CLPR:
6. The process according to claim 5 wherein the metal surface comprises copper.

CLPR:
7. The process according to claim 1 wherein the metal surface comprises copper.

CLPR:
8. The process according to claim 6 wherein the oxidizer is selected from the group consisting of hydrogen peroxide and persulfates.

CLPR:
18. The process of claim 15 wherein said compound is an alkali metal phosphate selected from the group consisting of sodium phosphate and potassium phosphate.

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L4: Entry 24 of 31 File: USPT Aug 6, 1991

DOCUMENT-IDENTIFIER: US 5037482 A
TITLE: Composition and method for improving adhesion of coatings to copper surfaces

ABPL:
A composition for cleaning and improving the adhesion characteristics of a copper surface (which is in turn adhered to an underlying substrate) so as to enable a coating, e.g., of photoresist, to be adhered easily and completely to the copper surface, the cleaning and adhesion promoting composition consisting essentially of an aqueous solution of an alkane sulfonic acid, a surfactant and an oxidizing agent of a type, and present in an amount, sufficient to provide controlled conversion of the copper surface to a substantially clean, micro-roughened surface, without removing the copper surface from the underlying substrate, so that the adhesion characteristics of the copper surface are substantially increased for receiving and securely adhering a subsequently applied coating.

BSPR:
The present invention relates to improving the adhesion characteristics of a copper surface to enable subsequently applied coatings to be completely and easily adhered to the copper surface and, more particularly, to an improved cleaning and adhesion promoter composition and method for treating the surface of copper foil laminates used in printed circuits to improve the adhesion of subsequently applied coatings affixed to the copper surface.

BSPR:
The composition of the invention removes contaminants from the copper surface (which in turn is adhered to an underlying substrate) and enhances the surface topography thereof by controlled conversion of the copper surface from a relatively smooth surface to a micro-roughened surface, through a microetching which removes, e.g., from about 0.5 to 5 microns of the copper. In this way, a copper foil laminate for use as a printed circuit board is provided with improved adhesion characteristics to enable subsequently applied photoresist or oxide coatings to more easily and completely adhere to the copper surface. More particularly, the invention relates to an improved cleaning and adhesion promoter composition which is capable of concurrently bringing about both cleaning and microetching of the copper surface to improve the adhesion characteristics of the copper surface prior to the application of photoresist or oxide coatings to the copper surface in the manufacture of printed circuit boards.

BSPR:
In a typical preparation of printed circuits, a copper foil is bonded to an insulating substrate which may be phenolic, epoxy, polyimide, polyester, or the like. The foil is normally treated electrolytically to provide a specific surface structure, such as disclosed in U.S. Pat. Nos. 3,293,109; 3,318,758; 3,518,168; 4,049,481; 4,131,517; 4,176,035; and others.

BSPR:
Multilayer printed circuit boards are assemblies containing several copper foil-clad substrate inner-layers, further bonded to each other through layers of semicured polymeric material, which are subsequently cured at elevated temperatures and pressures to form the complete laminate assembly. Prior to this assembly, the copper foil of the innerlayers is imaged and etched to form the innerlayer circuits of the assembly.

BSPR:
The printed circuit board industry is continuously faced with an increasing

demand for higher density circuitry. This has led to the production of finer lines of circuitry and is leading toward the use of thinner and thinner copper foils. As this trend continues, the preparation of the innerlayer copper foil becomes increasingly more critical. The use of thinner foils requires much tighter processing controls in order to produce uniform circuitry.

BSPR:
Combining the steps of initially cleaning and preparing a copper surface adhered to an underlying substrate to improve the adhesion characteristics of the copper surface for easily and completely affixing subsequently applied coatings would reduce the labor involved as well as the time to process the circuit boards. Thus, the final cost of manufacturing each board would be reduced.

BSPR:
While the present invention is particularly apropos of printed circuit board manufacture, and more particularly innerlayers of multilayered circuit boards, the need to remove contaminants from copper surfaces and to improve the adhesion characteristics of copper surfaces so that subsequently applied coatings will be more completely adhered to the copper surface also arises in other contexts where a contaminant-free surface with adhesion-improved characteristics of the copper surface is needed for subsequent plating operations for decorative or functional purposes.

BSPR:
Preparing copper innerlayer laminates previously involved several process steps to ensure a clean copper foil surface prior to application of photoresist and/or oxide coatings. The processes used in industry include a pumice or mechanical scrub usually followed by a chemical treatment of peroxide/sulfuric, or persulfate. Such processes have their own inherent problems: for example, when pumice is used there is pumice entrapment in the copper foil, or in the case of mechanical scrubbing with nylon brushes, gouging of the foil surfaces results. In addition, thinner innerlayer materials are susceptible to other defects and damage from aggressive mechanical surface scrubbing, such as distortion and incomplete treatment of copper surfaces due to worn scrubbers or plugged nozzles. The subsequent chemical treatment cannot overcome the damage done to the foil by these mechanical methods. Also, the regular chemical treatments are not effective in removing the chromate films on the foil that may remain after scrubbing, thereby resulting in a poor surface topography for the adhesion of the subsequently applied photoresist and/or oxide coatings.

BSPR:
In order to avoid some of the damaging effects of scrubbing, some manufacturers use a chemical cleaning method. In this instance the laminate is processed in an alkaline or acid cleaner traditionally known in the art, followed by a conventional chemical treatment (e.g., peroxide/sulfuric acid as above noted). The cleaners have the ability to remove the handling soils, fingerprints and oils that may be present on the laminate, but usually have little effect on the chromate film on the copper foils present from the lamination process. Again, the chemical treatment only partially removes the chromate film on the copper surface which in turn produces a less than satisfactory application of the subsequently applied photoresist or oxide coating because it does not adhere properly to the copper surface at the places where the chromate film residue remains.

BSPR:
A primary object of the present invention is to provide a composition useful for treating a copper surface, adhered to an underlying substrate, by removing contaminants from the copper surface and improving the adhesion characteristics of the copper surface to enable subsequently applied coatings to be more easily and completely adhered to the copper surface.

BSPR:
Another object of the invention is to provide a composition for concurrently removing contaminants from a copper surface, adhered on an underlying substrate, and for enhancing the surface topography of the copper surface of the laminate by controlled conversion of the substantially smooth copper surface to a substantially micro-roughened topography, thereby improving the adhesion characteristics of the copper surface for subsequently applied coatings.

BSPR:

Yet another object of the invention is to provide a composition for removing contaminants such as chromate and/or triazole tarnish inhibitor films as well as handling soils from a copper surface while concurrently treating the topography of the copper surface to achieve enhanced adhesion characteristics of the copper surface so that subsequently applied photoresist or oxide coatings are completely adhered to the copper surface.

BSPR:
Still another object of the invention is the provision of a composition of the type described which effects, in a single application step, the removal of contaminants from a copper surface and roughens the surface topography of the copper surface to provide better adhesion characteristics of the copper surface to insure that subsequently applied photoresist or oxide coatings are completely adhered to the copper surface.

BSPR:
These and other objects are achieved by the provision in the present invention of a composition and method for treating a copper surface, which is in turn adhered to an underlying substrate, the composition consisting essentially of an aqueous solution of an alkane sulfonic acid, a surfactant, and an oxidizing agent of a type, and present in an amount, to provide in cooperating interaction with the surfactant a cleaning of the copper surface and a controlled conversion of the copper surface from a substantially smooth surface to a substantially micro-roughened surface topography so that the copper surface has increased adhesion characteristics for coatings subsequently applied to the copper surface and without removing said copper surface from the underlying substrate. In the preferred embodiment, the composition consists essentially of between about 5% and 60% by weight of the alkane sulfonic acid, between about 0.01% and 50% by weight of the oxidizer, and between about 0.001% and 10% by weight of the surfactant.

BSPR:
In the preferred embodiment of the invention, the alkane sulfonic acid comprises methane sulfonic acid, the oxidizer comprises ferric nitrate, and the surfactant comprises a nonionic and/or anionic surfactant.

BSPR:
The foregoing composition is effective not only in removing soils and the like (e.g., the chromate and/or triazole tarnish inhibitor films present on copper foil-clad substrates by reason of the copper foil lamination process), but concurrently also in roughening the surface by converting the substantially smooth copper surface to a substantially uniformly micro-roughened copper surface by means of a microetching of from about 0.5 to 5 microns of the copper thickness to enhance the adhesion characteristics of the copper surface for the subsequent application thereto of coatings such as photoresist or oxide coatings.

DRPR:
FIG. 1 is an electron-microscope-generated photograph showing the surface of copper foil before being treated by the cleaning adhesion promoter composition at a magnification of 5000.times. and at a 45.degree. angle to surface to show the surface topography;

DRPR:
FIG. 2 is an electron-microscope-generated photograph at the same magnification and at a 45.degree. angle to surface as FIG. 1, showing the surface topography of copper foil after being treated by the method of this invention as set forth in Example 1; and

DRPR:
FIG. 3 is an electron-microscope-generated photograph at a magnification of 4500.times. and at a 45.degree. angle to surface showing the surface topography of copper foil treated by a prior art method according to Example 3 of U.S. Pat. No. 4,632,727.

DEPR:
In accordance with the present invention, a combination cleaner and adhesion promoter composition is provided to act as a pretreatment for a copper surface adhered to an underlying substrate so as to remove contaminants such as soils, fingerprints, triazole tarnish inhibitor and chromate films from the surface of

the copper and to provide improved surface topography on the copper surface which will improve the bonding of any subsequently applied photoresists (i.e., both liquid or dry-film type) or oxide coatings to the copper surface.

DEPR:
This cleaning and adhesion promoting composition performs two functions simultaneously when applied to the copper surface adhered to an underlying substrate. First it cleans the copper surface being treated by removing any contaminants on the surface, such as for example soils, fingerprints, triazole tarnish inhibitor, chromate films, and the like. Then, it converts the substantially smooth copper surface through a controlled reaction to a substantially uniformed micro-roughened surface topography to thereby further improve the bonding adhesion characteristics of the treated copper surface to enable subsequently coatings to be easily and completely adhered to the copper surface. Examples of subsequently applied coatings used in the manufacturing of printed circuit boards are photoresists (i.e. both liquid or dry film type) and/or oxide coatings. A copper foil laminate is but one example of a copper surface that may be so treated by this cleaning and adhesion promoting composition.

DEPR:
The cleaner/adhesion promoter is composed of water, alkane sulfonic acid (generally either methane or ethane sulfonic acid), an oxidizing agent for copper, and specific surfactants. The alkane sulfonic acid is used from about 5% to about 60% by weight of the composition, preferably from about 15% to about 40% by weight. The oxidizer can range from about 0.1% to about 50% by weight of the composition, preferably from about 1% to about 15% by weight, and most preferably from about 5% to about 10% by weight, all of course depending upon the type of oxidizing agent employed. The oxidizers can include ferric nitrate, peroxide, ferric chloride, and copper chloride, with ferric nitrate preferred. The surfactants range from about 0.001% to about 10% by weight of the composition, preferably from about 0.01% to about 3% by weight. The surfactants alone or in combination, preferably encompass nonionic and anionic surfactants. Examples of nonionic surfactants include without limitation: ethoxylated nonyl- and octlylphenols of ethylene oxide from 3 to 30 moles of ethylene oxide, preferably 3.5 moles, and modified polyethoxylated straight chain alcohols as are available under tradename Triton DF-16 from Rohm & Haas; alkyl polyoxyalkylene ether, e.g. Mazawet DF from Mazer Chemical; and block copolymers of ethylene oxide and propylene oxide such as Pluronic 31R1 from BASF. Anionic surfactants include without limitation: sulfonated aryl and alkyl hydrocarbons such as Petro BA from Desoto, Inc.; sulfated aryl and alkyl hydrocarbons such as Sipon BOS from Alcolac, Inc.; and phosphate esters such as Triton H-66 from Rohm & Haas.

DEPR:
The cleaner/adhesion promoter composition is generally used at a temperature ranging from about ambient to about 130.degree. F. with a preferable range being from 80.degree. F. to 95.degree. F., from a contact time of from about 10 seconds to 10 minutes, preferably from 30 seconds to 5 minutes. When the composition is used with peroxide, ferric chloride or copper chloride as the oxidizer, these materials are consumed in the reaction which remove copper from the copper surface. Thus, using these compounds necessitates regular additions of the oxidizers to maintain continuous operation. When ferric nitrate is used, the oxidizer is lost only by drag-out. It is theorized that upon reacting and removing copper from the copper surface, the iron is re-oxidized from ferrous to ferric and is available to again remove more copper. Thus, the only limiting factor in the cleaner/adhesion promoter in this regard is its capacity to hold copper in solution.

DEPR:
The oxidizer must be of a type, and present in an amount, sufficient to provide in cooperating interaction with the surfactant, a controlled conversion of the copper surface from a substantially smooth surface to a substantially clean, substantially uniformly micro-roughened surface, so that the bonding characteristics of the copper surface are substantially increased for securely adhering a subsequently applied coating to the copper surface, without at the same time removing the copper surface itself from the underlying substrate to which it is adhered. An oxidizing agent which is too active, and/or which is used in too substantial concentrations, not only runs the risk of uncontrolled stripping of the copper surface from its underlying substrate, but more

importantly has been found ineffective to produce the required micro-roughened topography on the remaining copper surface. Results such as this have been found with compositions containing nitric acid as the oxidizer. Even where complete stripping is avoided, the remaining copper surface is nevertheless surprisingly smooth and unacceptable for promoting adhesion of subsequently applied coatings.

DEPR:
The cooperating interaction of a suitable oxidizer, used in suitable amount, along with the surfactant, provides a controlled cleaning and conversion of the substantially smooth copper surface to a substantially micro-roughened, clean surface, with between about 0.5 and 5 microns of the original copper surface being removed. This micro-roughening provides increased surface area, thereby improving the bonding characteristics of the treated copper surface, especially to subsequently applied coatings.

DEPR:
The alkane sulfonic acid in the cleaner/adhesion promoter composition according to the present invention is selected from any one or more compounds having the formula RSO.sub.3 H, where R is a lower alkyl group having from 1 to 5 carbon atoms, and preferably 1 or 2 carbon atoms, i.e., methane sulfonic acid or ethane sulfonic acid, with methane sulfonic acid most preferred.

DEPR:
The amount of alkane sulfonic acid employed in the aqueous compositions is preferably in an amount ranging from 3% to 45% by volume, more typically 10% to 40% by volume, and most typically 25% to 30% by volume, based upon a 70% methane sulfonic acid aqueous solution, which is a form in which methane sulfonic acid is commonly sold. Obviously, however, other concentrations, and the anhydrous form of the acid, can be used in making up the composition.

DEPR:
The present invention also affords a means for regenerating the bath per se or any removed portion thereof both to recover metal values and to reestablish operating concentrations of the alkane sulfonic acid.

DEPR:
As indicated earlier, the composition of the invention provides for the removal of contaminants, such as dirt, soils and chromate and thiazole tarnish inhibitors, from the copper surface and provides a fine uniform etch with good topography to enhance photoresist or oxide adhesion to the surface of the copper. For one ounce copper-clad innerlayers (.0014 inches of copper), best results occur when the composition effects removal of from between 0.5 microns (0.00001 in) to 5 microns (0.0002 in) of the copper. The composition may be applied by immersion, spraying or other modes.

DEPR:
Not only are the contaminants removed from the surface of the copper foil but the copper surface topography itself undergoes a change--that is, the substantially smooth surface is micro-roughened by a controlled conversion to a substantially clean, substantially uniformly roughened surface topography. Compare FIGS. 1 and 2. Note that in FIG. 2 the number and magnitude of the irregularities on the copper surface is increased using the composition of the invention. Such action increases the surface area of the copper available for bonding and thus promotes better adhesion to the copper surface of a subsequently applied coating.

DEPR:
A 7 mil core, 1 oz. copper laminated epoxy innerlayer was processed through an immersion cleaner/micro-etch prior to dry-film photoresist lamination. The process using the steps set forth below was as follows:

DEPR:
The amount of copper removed was approximately 1.25 microns (0.00005 inches) from the copper foil surface.

DEPR:
Upon inspection after the alkaline etching of the 1 oz. of copper in non-resist areas to define the innerlayer circuitry, no lifting of the photoresist was evident. The surface of the foil before and after treatment with the cleaner/micro-etch is shown in the electron-microscope-generated photographs

labeled FIGS. 1 and 2, respectively. The micro-roughened surface with numerous deep irregularities and an average vertical depth penetration of 1.25 microns is shown in FIG. 2 as contrasted with the untreated copper surface of FIG. 1 which is substantially smooth and has a relatively even and unbroken copper surface topography.

DEPR:
The same process as used in Example 1 was utilized and repeated except that the cleaner/adhesion formulation was as follows. (i.e., no surfactants were employed):

DEPR:
Inspection of the laminate prior to dry-film lamination showed a splotchy copper surface indicative of uneveness of the surface topography. Inspection after dry-film and alkaline etch revealed an undesirable lifting of the dry-film in areas corresponding to the location of the splotchy areas on the copper foil surface.

DEPR:
This etchant solution was used at 95.degree. F. (approx. 34.degree. C.) versus 45.degree. C. as indicated in the Nelson patent. The time of etching was reduced to 24 seconds. The action of this composition was very aggressive, but did not provide a proper topography of the copper surface. FIG. 3 shows the unacceptable smooth topography resulting from this treatment, while FIG. 2 shows the preferred enhanced substantially micro-roughened surface topography resulting from the application of the cleaner/adhesion promoter composition of the invention.

DETL:
Water 57.325% by weight Methane Sulfonic Acid (70%) 35.0% by weight Ferric Nitrate 7.5% by weight Mazawet DF 0.05% by weight Triton DF-16 0.075% by weight Petro BA 0.05% by weight

DETL:
Water 57.5% by weight Methane Sulfonic Acid 70% 35.0% by weight Ferric Nitrate 7.5% by weight

DETL:
Distilled Water 1100 cc Methane Sulfonic Acid 70% 1000 cc Nitric Acid 70% 900 cc Reten 520 (2% solution) 100 cc (A Hercules Polyacrylamide) Varion H.C. 5 cc (A Sherex Chemical Surfactant)

CLPR:
1. A process for cleaning and improving the adhesion characteristics of a copper surface, adhered to an underlying substrate, for enabling a subsequently applied coating to be easily and completely adhered to the copper surface, said process comprising contacting said copper surface with a composition consisting essentially of water, an alkane sulfonic acid, a surfactant, and an oxidizing agent for copper, said oxidizing agent being of a type, and present in an amount, sufficient to provide, in cooperating interaction with the surfactant, and under the conditions and time of said contacting, controlled conversion of the copper surface to a substantially clean, substantially uniformly micro-roughened surface without etching said copper surface from said underlying substrate, whereby the adhesion characteristics of said copper surface are substantially increased for receiving and securely adhering a subsequently applied coating thereto.

CLPR:
2. The process according to claim 1, wherein said alkane sulfonic acid is present in an amount of from about 5% to 60% by weight; said oxidizer is present in an amount of from about 0.1% to 60% by weight; and said surfactant is present in an amount of from about 0.001% and 10% by weight.

CLPR:
3. The process according to claim 2 wherein said surfactant is a mixture of nonionic and anionic surfactants.

CLPR:

4. The process according to claim 1, wherein said nonionic surfactant is selected from the group consisting of ethoxylated nonylphenols and octylphenols and alcohols of ethylene oxide, alkyl polyoxyalkylene ether, and block copolymers of ethylene and propylene oxide; and the anionic surfactant is selected from the group consisting of sulfonated aryl and alkyl hydrocarbons, sulfated aryl and alkyl hydrocarbons, and phosphate esters.

CLPR:
5. A process for cleaning and improving the adhesion characteristics of a copper surface adhered to an underlying substrate, for enabling a subsequently applied coating to be easily and completely adhered to the copper surface, said process comprising, contacting said copper surface with a composition consisting essentially of water, methane sulfonic acid, ferric nitrate, and a surfactant mixture of ethoxylated nonyl- and octylphenols and alcohols of ethylene oxide, alkyl polyoxyalkylene ether, and sulfonated aryl and alkyl hydrocarbons, for a time and at conditions effective to provide a controlled conversion of the copper surface to a substantially clean, substantially uniformly micro-roughened surface topography without removing said copper surface from said underlying substrate.

CLPR:
6. A process according to claim 5 wherein said composition consists essentially of water, between about 15%-40% by weight of an alkane sulfonic acid selected from the group consisting of methane sulfonic acid and ethane sulfonic acid; between about 1%-15% by weight of an oxidizer selected from the group consisting of ferric nitrate, peroxide, ferric chloride, and copper chloride; and between about 0.01%-3% by weight of a surfactant selected from the group consisting of nonionic surfactants and anionic surfactants, and mixtures thereof.

CLPR:
7. A process according to claim 6 wherein said composition consists essentially of water, about 35% by weight of an methane sulfonic acid (70%), about 7.5% by weight of ferric nitrate, and about 1.75% by weight of a surfactant mixture of ethoxylated nonyl- and octylphenols and alcohols of ethylene oxide, alkyl polyoxyalkylene ether, and sulfonated aryl and alkyl hydrocarbons.

CLPR:
8. The process according to claim 3 wherein said step of contacting said surface with said composition is achieved by immersing said copper surface in said composition.

CLPR:
9. The process according to claim 3 wherein said step of contacting said surface with said composition is achieved by spraying said composition onto said copper surface.

CLPR:
10. The process according to claim 3 wherein said copper surface is a copper-clad printed circuit board substrate.

CCOR:
134/3

CCXR:
134/41

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L4: Entry 30 of 31 File: USPT Sep 6, 1977

DOCUMENT-IDENTIFIER: US 4046620 A
TITLE: Process for improving the solderability of electric circuit boards

ABPL:
A process is provided for improving the solderability of electric circuit boards with conductor paths composed of copper or copper alloys, in which, at least at the locations to be soldered, the conductor paths are cleansed in a first solution and are thereby deoxidized, and are then activated in a second solution.

BSPR:
Following the completion of circuit boards provided with conductor paths consisting of copper or copper alloys, residues and impurities resultant from the production give rise to difficulties regarding the solderability of the conductor paths which are further increased as a result of a long storage of the circuit boards. Experience has shown that the best remedy regarding soldering faults is provided by a careful and suitable cleansing of the circuit boards and the subsequent application of a soldering agent. To this end, the surfaces of the conductor paths can be freed of impurities mechanically by sand-blasting, scouring, grinding, buffing, brushing and even by erasing with a special rubber. However, in these mechanical cleansing processes, it is difficult to control the extent of the removal of metal from the surface of the conductor paths. In addition, particles of the grinding agents which are employed and also of the abraded material can settle at points to which it is difficult to gain access and can impair a subsequent soldering.

BSPR:
For this reason generally, chemical cleansing processes are given preference. Thus, the U.S. Pat. No. 3,020,175 discloses a chemical cleansing process for electric circuit boards in which the surfaces of the conductor paths are freed of dirt and oxides in a first acid oxidizing solution, for example, a mixture of chromic acid and sulphuric acid. Subsequently, the surface of the conductor paths is activated, i.e. brought into a condition of good solderability, in a second solution, for example, dilute hydrochloric acid. In this second solution salt films, such as, for example, chromate films which have formed during the treatment in the first solution, are completely removed. The improvement in solderability which is achieved with this chemical cleansing process reduces considerably, however, with increasing length of storage of circuit boards after such a treatment. Furthermore, the baths employed in chemical cleansing processes not only require expensive servicing, but also are generally very agressive and complicated to prepare in respect of environmental waste disposal technology.

BSPR:
For the realisation of this aim, the invention proposes a two solution circuit board contacting process in which an aqueous solution of non-ionic surfactant and an organic acid is used as a first solution, and an aqueous solution of potassium persulfate (potassium peroxydisulfate) and an acid is used as second solution.

DEPR:
Surfactants are to be understood as water-soluble compounds active at bundary surfaces, a molecule of which possesses at least one hydrophilic component and a hydrophobic remainder. In non-ionic surfactants, the hydrophilic component of the molecule is the location of an electro-neutral group. In non-ionic surfactants, the hydrophilic component of the surfactant molecule is achieved either through the presence of oxygen in the molecule (as in ethylene oxide or propylene oxide hydrophylic linkages, terminal hydroxyl groups, or oxygen linked directly to

nitrogen as in amide groups) or via sulfonate, phosphate, or carboxylate terminal groups in the case of zwitterionics. The hydrophobic component of a non-ionic surfactant molecule comprises hydrocarbon chains which can be linked to such a hydrophilic component via aliphatic or aromatic ring systems.

DEPR:
Preferably, in accord with the teachings of this invention, a first solution contains a non-ionic surfactant of the ethoxylated type. Ethoxylated surfactants are formed by condensing ethylene oxide to form polyether chains using the so-called ethoxylation reaction. If this reaction occurs with a substance which possesses hydrogen atoms which are capable of reacting, for examples, with a fatty acid or a phenol, in the presence of either acidic or basic catalysis, polyether chains develop whose end groups are hydroxyl groups, for example: ##STR1##

DEPR:
In ethoxylation, compounds such as, for examples, fatty acids, aliphatic alcohols, fatty amines, fatty acid amides, alkyl substituted phenols and other phenol homologs, aliphatic mercaptans, terpene alcohols, or the like, are reacted with ethylene oxide. For purposes of the present invention, one commences with compounds which contain from about 10 to 18 carbon atoms per molecule in the form of hydrophobic chains. Sufficient ethylene oxide is condensed per molecule therewith to achieve a "degreee of ethoxylation" corresponding to from about 2 to 40 Moles ethylene oxide. The "degree of ethoxylation" does not define a clear chain length since, as with all polymers, actual chain length in a given product is statistically distributed about a mean value. Examples of suitable non-ionic ethoxylated surfactants include alkyl ethoxylates, ethoxylated alkyl phenols, fatty acid ethanol amides, polymers of ethylene oxide, propylene oxide, and alcohols, and the like, all having incorporated thereinto from about 2 to 40 moles of ethylene oxide per molecule.

DEPR:
Advantageously, a first solution with ethoxylated alkyl phenol is used as the non-ionic surfactant. When, for example, an aqueous solution comprising from about 20 to 100 grams of ethoxylated alkyl phenol per liter and from about 15 to 80 grams of an organic acid per liter is used as the first solution, an excellent cleansing and a reliable deoxidation of conductor paths on circuit boards is ensured in a first treatment stage of the process of the invention. The first solution is preferably adjusted with such organic acid so as to have a pH of about 2.

DEPR:
The use of a second solution saturated with potassium persulfate has proven to be particularly advantageous. Preferably, such a second solution is adjusted to have a pH-value of between about 2.0 and 4.0 by the addition of sulphuric acid, and thereafter preferably such solution is stabilized against decomposition with concentrated phosphoric acid. The amount of phosphoric so added in solution form ranges from about 0.1 to 0.5 grams per liter. The circuit board surfaces activated with a second solution of this type are characteristically light in color and possess a uniform smoothness, and during subsequent soldering display excellent wetting characteristics with a uniform solder distribution.

DEPR:
Thus, to improve the solderability of a circuit board with conductors composed of a copper or copper alloys, in accordance with this invention, one first contacts with a first solution (preferably by immersion of the circuit board to be treated) conductor paths on such a board at least in areas thereof to be soldered. Contact time typically ranges from about 1 to 5 minutes, though longer and shorter contact times may be used.

DEPR:
The first solution used in such a contacting preferably comprises on a 100 weight percent total weight basis from about 2 to 20 weight percent of at least one dissolved non-ionic surfactant, from about 1 to 20 weight percent of at least one dissolved organic acid capable of producing a pH of not larger than 2 in water solution at a concentration of less than 50 grams per liter, and the balance up to 100 weight percent of any given first solution being water.

DEPR:

The second solution employed for such a second contacting preferably comprises on a 100 weight percent total weight basis from about 0.5 weight percent up to solution saturation of dissolved potassium persulfate, sufficient added sulfuric acid to produce in any given such solution a pH of from about 1 to 4, from and including 0 up to about 0.5 weight percent of dissolved phosphoric acid, and the balance up to 100 weight percent of any given such second solution being water,

DEPR:
A preferred class of such organic acids comprises lower alkanoic acids (e.g. those containing less than seven carbon atoms per molecule). A more preferred such acid comprises formic acid.

DEPR:
In order to achieve optimum results, it is necessary to monitor the solutions employed. The first solution charcteristically has a practically unlimited life. However, it is advisable to monitor the density and the pH value of the first solution at intervals. Deviations from starting density can be corrected with addition of an aqueous concentrate of surfactant and/or organic acid. Evaporation losses are compensated for by adding tap water to a first solution. If after a long period of use, considerable clouding of a first solution through build-up therein of particles of dirt may be noticed, and, if so, it is advisable to discard the preparation.

DEPR:
As a result of contact with the conductor paths composed of copper or copper alloys in circuit boards, a second solution is gradually consumed until a maximum copper absorption for a given second solution is achieved. Second solution density increases through contact with circuit boards to some maximum value which is dependent upon the particular second solution employed. Thus, the second solution loses its effectiveness. The bath monitoring of the second solution consists simply in checking the density and the pH value at intervals. Evaporation losses in a second solution are compensated for by adding tap water thereto. Second solution pH value tends to rise through use, and this is compensated for by adding small amounts of diluted sulfuric acid thereto.

DEPR:
The elimination of the first and second solutions using environmental waste disposal technology is effected by emptying the spent solutions or baths into a concentrate container of a waste water plant effluent system and then neutralizing such with caustic potash and/or caustic soda. The released copper ions are then precipitated as copper hydroxide by which the majority of the surfactants is absorbed. The surfactants and the formic acid are oxidized by the perioxide to form carbon dioxide.

DEPR:
Following their production, circuit boards are submerged into a first solution for a length of time between about 1 an 3 minutes, and are subsequently slowly withdrawn therefrom in order to keep the discharge of adhering liquid small. The temperature of the first solution, which characteristically depends upon the pollution associated with the circuit boards, generally corresponds approximately to room temperature. The first solution here comprises one liter of tap water in which is dissolved both 25 grams of ethoxylated alkyl phenol with a degree of ethoxylation of from about 8 to 14 and 20 grams of 100% formic acid.

DEPR:
Following a flushing treatment of about 12 seconds duration in room temperature tap water, the circuit boards are submerged into a second solution. The surfaces of the circuit boards are then activated in this second solution at room temperature without moving or agitation of the system. The period of dwell of the circuit boards in this second solution amounts to about 5 minutes. The second solution is prepared by dissolving potassium persulfate salt at the rate of 54 grams per liter of tap water at a water temperature of 20.degree. C. followed by adding thereto about 10% sulphuric acid. The quantity of sulphuric acid so added is sufficient to produce in the resulting solution a pH value of 2. For the purposes of stabilization, 0.5 gram per liter of concentrated orthophosphoric acid (H.sub.3 PO.sub.4) is added to the preparation.

DEPR:
The solutions employed are monitored. The first solution is found to have a

practically unlimited life. The first solution appears to have an optimum starting density of about 1,004 g/cm.sup.3 and 0.7.degree.Be (degree-Baume) and an optimum pH value of 2. Deviations are corrected by addition of fresh solution, or by addition of concentrated formic acid. Evaporation losses are compensated for by adding tap water to the first solution. After a long period of use, considerable clouding of the first solution through particles is noticed, and this used solution is discarded.

DEPR:
When freshly made, the second solution possesses a starting density of 1.033 g/cm.sup.3 or 4.9.degree.Be and a pH value 2. As a result of contact with the conductor paths composed of copper or copper alloys in circuit boards, such solution is gradually consumed until a maximum copper absorption of 12 g/l and a corresponding density of the solution of 1.057 g/cm.sup.3 or 7.9.degree.Be is observed. Thus, the second solution loses its effectiveness. The bath monitoring of the second solution consists in checking the density and the pH value at intervals. Evaporation losses are compensated by supplying tap water to such second solution. The pH value of such second solution is corrected by adding thereto small quantities of diluted sulphuric acid. To ensure sufficient reliability of this second solution for the activation of circuit boards, this second solution is discarded when its density reaches a value of 1.054 g/cm.sup.3 or 7.5.degree.Be.

CLPR:
1. A process for improving the solderability of a circuit board with conductor paths composed of copper, or copper alloy comprising the steps of

CLPR:
2. The process of claim 1 wherein said non-ionic surfactant is ethoxylated.

CLPR:
3. The process of claim 2 wherein said surfactant is selected from the group consisting of alkyl ethoxylates, ethoxylated alklyl phenols, fatty acid ethanol amides, and polymers of ethylene oxide, propylene oxide, and alcohols, said surfactant containing from 2 to 40 moles of ethylene oxide per molecule.

CLPR:
4. The process of claim 3 wherein said surfactant is an ethoxylated alkyl phenol.

CLPR:
5. The process of claim 1 wherein said organic acid is a lower alkanoic acid.

CLPR:
6. The process of claim 5 wherein said lower alkanoic acid is formic acid.

CLPR:
7. The process of claim 1 wherein said non-ionic surfactant is an ethoxylated alkyl phenol having a degree of ethoxylation of from about 8 to 14 employed at a concentration of from about 20 to 100 grams per liter and said organic acid is formic acid employed at a concentration of from about 15 to 80 grams per liter, the quantity of said organic acid being used being at least sufficient to produce a pH of about 2, said first solution having a starting density of about 1.004 grams per cubic centimeter.

CLPW:
from about 2 to 20 weight percent of at least one dissolved non-ionic surfactant,

CLPW:
from about 1 to 20 weight percent of at least one dissolved organic acid capable of producing a pH of not larger than 2 in water solution at a concentration of less than 50 grams per lite, and

CLPW:
from about 0.5 weight percent up to solution saturation of dissolved potassium persulfate

CLPW:

sufficient added sulfuric acid to produce therein a pH of from about 1 to 4,

CLPW:
from and including 0 up to about 0.5 weight percent dissolved phosphoric acid, and

CCXR:
134/3

CCXR:
134/41